



TITLE:

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9. Bond Energies and Reactivity of Radicals. (I)

A New Expression of Bond Energies of Organic Compounds

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INTRODUCTION

Bond energies, about which Pauling's detailed study¹⁾ was already remarkable, are the most important character of organic or inorganic compounds from the viewpoint of the reactivity. The present author has invented an empirical expression concerning bond energy of organic compounds and suggested a convenient scale for the polarity and the unstability or the reactivity of radicals, by use of which the reactivity of organic reaction will be able to be explained.

Pauling proposed an equation for average bond energy between atoms, assuming the co-valent nature of symmetrical bond, *i. e.* A-A or B-B, and its additive character. The bond energy between hetero atoms A-B, which is referred to D_{AB} , is found always greater than the mean value of symmetrical bond, such as D_{AA} and D_{BB} . It is due to the contribution of ionic nature of hetero bond. He has also found the additive rule in the square root of such differences and suggested the following formula for bond energy between hetero atoms :

$$D_{AB} = \frac{1}{2}(D_{AA} + D_{BB}) + k(X_A - X_B)^2 \quad (1)$$

where X_A and X_B are the characteristic quantities of atoms A and B respectively, named by Pauling electronegativities. They represent the electron seeking tendency of atoms in chemical bond and are considered to be in close connection with ionization potential, electron affinity of atoms or dipole moment of chemical bond. The validity of Pauling's electro-negativity scale is often confirmed actually by many chemists.

A NEW EXPRESSION OF BOND ENERGIES

Another expression of bond energy especially in organic compound, which is ultimately equivalent to Pauling's one, has been proposed by the author²⁾. As seen in molecules, the similar polarization may be brought about also in atoms by the effect of electronegative nature of nucleus, which attracts electron cloud to itself. The bond energy (D_{AB}) between such polarized atoms A and B can be expressed in terms of the covalent and the electrostatic energies as follows :

* 古川 淳二

$$D_{AB} = J_A + J_B - e_A e_B \quad (2)$$

where J and e denote the scales of covalent energy and the polarity of the atom. The bond energies of organic compounds are listed in Table 1, many of which are quoted mainly from Szwarc's review³⁾. The data are presented in kcal. per mole (the values in parentheses are explained later). The data in the upper part on the left side of the Table, which are concerned in carbon-carbon bond, were calculated, neglecting the polar term on account of the neutral nature of carbon atom. The differences between corresponding ranks or files give nearly constant values, and this fact suggests the bond energy in this case to be represented in the form of the sum of characteristic value of J . This is easily understood from the following.

| | A | B | C |
|------------|---------------|---------------|---------------|
| A | $J_A + J_A$ | $J_A + J_B$ | $J_A + J_C$ |
| Difference | $(J_A - J_B)$ | $(J_A - J_B)$ | $(J_A - J_B)$ |
| B | $J_B + J_A$ | $J_B + J_B$ | $J_B + J_C$ |
| Difference | $(J_B - J_C)$ | $(J_B - J_C)$ | $(J_B - J_C)$ |
| C | $J_C + J_A$ | $J_C + J_B$ | $J_C + J_C$ |

The mean value of these differences gives the probable relative scale of J -values, but its absolute values are still unknown. It is reasonable to determine the absolute J -values, by taking a half of symmetrical bond, $1/2 D(\text{CH}_3\text{CH}_3)$ and, $1/2 D(\text{C}_2\text{H}_5\text{C}_2\text{H}_5)$ as the J -values of $J(\text{CH}_3)$ and $J(\text{C}_2\text{H}_5)$, respectively.

Whence several values of J are given as follows :

$$J(\text{CH}_3) = 41.5, J(\text{C}_2\text{H}_5) = 41.5, J(\text{CH}_2 = \text{CH}\cdot) = 50, J(\text{CH} \equiv \text{C}\cdot) = 69 \text{ kcal. etc.}$$

The bond energies of hydrogen compounds have not such simple additive relationship because of the larger polar nature. The similar polarity needs to be taken into consideration with the bond energies of chlorine, bromine, iodine, hydroxyl, amino and cyano radicals to obtain the good accordance between experimental and calculated values. Such polar term can be calculated by the following methods.

a) If D_{AA} , D_{BB} and D_{AB} are known, they are written as

$$D_{AB} = J_A + J_B - e_A e_B$$

$$D_{AA} = 2J_A - e_A^2$$

$$D_{BB} = 2J_B - e_B^2$$

it follows that

$$(e_A - e_B)^2 = D_{AB} - (D_{AA} + D_{BB})/2$$

b) If D_{BB} , D_{AB} , J_A and e_A are known, they are written as

$$D_{BB} = 2J_B - e_B^2$$

$$D_{AB} = J_A + J_B - e_A e_B,$$

it follows that

$$e_B = \frac{1}{2} \left\{ e_A - \sqrt{e_A^2 - 4(2J_A + D_{BB} - 2D_{AB})} \right\}$$

c) If D_{AB} , D_{AO} , J_B , J_O , e_B and e_O are known, from following equations

$$D_{AB} = J_A + J_B - e_A e_B$$

$$\text{and } D_{AO} = J_A + J_O - e_A e_O,$$

it follows that

$$e_A = \frac{(J_B + J_O) - (D_{AB} - D_{AO})}{(e_B - e_O)}.$$

The reasonable values of J and e which are given in Table 2, are obtained from the average value calculated from the above equations. Since many of the bond energies, however, are not yet known enough, J is obliged to estimate neglecting e -value in these cases. The values in the Table are consequently not correct except for those of the first file. The values calculated from J and e in Table 2 are put in brackets in Table 1, which seem to be in accord with experimental data. The J and e values of radicals can be used not only for computation of unknown bond energy but also for estimation of the polar nature and the unstability of radicals. The polar nature of OH, NH_2 , Cl or Br is represented by the great negative e -value as is experimentally expected. Further the unstability of CH_3 , C_2H_5 , phenyl or OH radical, which has the great J -value, and the stable nature of *tert*-butyl, allyl or benzyl radical, which has the small J value, are also in accord with experience. The relation between reactivity and J and e values of radicals will be discussed later.

AVERAGE BOND ENERGY OF ATOMS AND ITS EXPRESSION BY J - e SCHEME

The average bond energy of atoms, for which Pauling suggested the empirical expression in the form of equation (1), is also represented by J - e scheme. Table 3 gives the average bond energies and calculated value from J - e scheme, the latter is written in parenthesis. The accordance of both values is fairly good. The e -value corresponds to the Pauling's electronegativity; the former is parallel to the latter, but it should be noted that the former is estimated by taking the carbon atom as the neu-

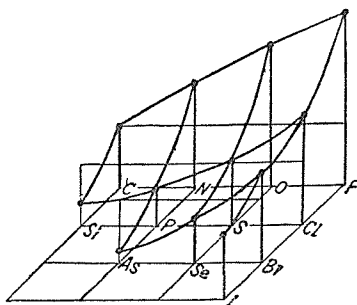


Fig. 1.

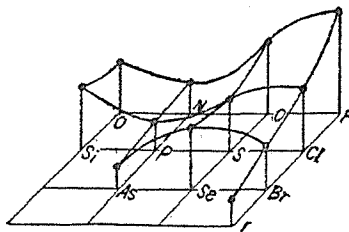


Fig. 2.

Table 1. Bond energies and their calculated values.

(kcal/mole, J in kcal/mole, e in (kcal) $^{1/2}$)


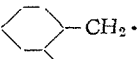
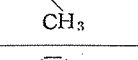
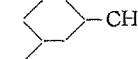
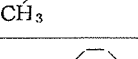
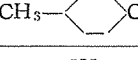
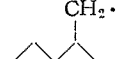


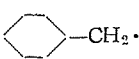
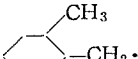
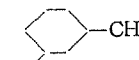
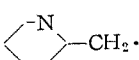
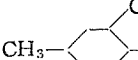
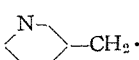
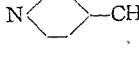
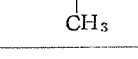
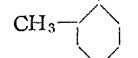

| | H• | CH ₃ • | C ₂ H ₅ • | $\frac{\text{CH}_2}{\text{CH}}\cdot$ | CH≡C• | <i>n</i> C ₃ H ₇ • | <i>i</i> C ₃ H ₇ • | $\frac{\text{CH}_2}{\text{CH}\cdot\text{CH}_2}\cdot$ | φ• | φCH ₂ • | <i>n</i> C ₄ H ₉ • | <i>i</i> C ₄ H ₉ • | •CHO | CH ₃ CO• | •Cl | •Br | •I | •OH | •NH ₂ | •CN | •NO ₂ | •NO | •SH | •SCH ₃ | •SC ₂ H ₅ | C ₆ H ₅ CO ^{***} | |
|--|--------------|-------------------|---------------------------------|--------------------------------------|---------------|--|--|--|---------------|--------------------|--|--|--------------|---------------------|--------------|----------------------|--------------|------------------|------------------|---------------|------------------|------------|--------------|-------------------|---------------------------------|---|------|
| <i>J</i> | 56 | 41.5 | 41.5 | 50 | 69 | 39 | 34 | 20 | 54 | 23 | 34 | 30 | 33.5 | 35 | 32 | 25 | 15 | 46 | 44 | 63 | 12 | 2? | 30 | 30 | 27 | 30.7 | |
| <i>e</i> | 2.8 | 0 | 0 | 0 | ? | 0 | 0 | 0 | +2 | 0 | 0 | -0.2 | +3.3 | +3.3 | -2 | -0.3 | +1 | -6 | -5.2 | -2.5 | +1 | 0 | 0? | 0 | 0 | 0 | +2.5 |
| H• | (104) 104 | (97.5) 101 | (97.5) 98 | (116) 104? | (125) 121? | (95) 95 | (90) 89? | (76) 77 | (104) 104? | (74) 77.5 | (90) 94 | (87) 85? | (79) 78 | | | | | (120) 115~118 | (125) 124~164 | (127) 121? | | | (86) 78? | | | (79.7) 78.8 | |
| CH ₃ • | (97) 101 | (83) 83 | (83) 82 | (91) 90? | (110) 110? | (80) 79 | (75) 74.5 | (61) 60 | (89) 94 | (64) 63 | (76) 78 | (73) 74? | (75) 75 | (76) 77 | (73.5) 74 | (76) 66 | (56.5) 54 | (88) 90,91 | (85) 79 | (105) 105 | (54) 57 | | (72) 74.2 | (72) 73.2 | (69) 70.6 | (72.2) 71.7 | |
| C ₂ H ₅ • | 97 | 82 | (83) 82 | (91) 90? | (110) 109? | (80) 79 | (75) 75? | (61) 60.5 | (90) 94? | (64) 62 | (76) 78 | (73) 73? | (75) 71 | (76) 77? | (72) 80? | (76) 65 | (56.5) 51 | (88) 90,93 | (85) 78 | | (54) 52 | | (72) 73.5 | (72) 71.8 | (69) 69.3 | | |
| CH ₂ =CH• | 104? | 90? | 90? | (100) 104? | | (89) 87? | (84) 85? | (70) 68.5? | (104) 104? | (73) 101? | (84) 86? | (80) 81? | (87) 84 | | | 8? | (68) 55 | (96) 91? | | (113) 121? | | | | | | | |
| CH≡C• | 121? | 110? | 109? | | | (108) 106? | (103) 103? | | (121) 119? | | | | | | | | | | | | | | | | | | |
| <i>n</i> C ₃ H ₇ • | 95 | 79 | 79 | 87? | 106? | (78) 76 | (73) 72? | (57) 57.5 | (92) 88? | (52) 59 | | | | | (71) 77 | | (54) 50 | (85) 92 | (83) 77 | | | | (69) 72.1 | (69) 69.7 | (66) 67.7 | | |
| <i>i</i> C ₃ H ₇ • | 89? | 74.5? | 75? | 85? | 103? | 72? | (68) 66.5 | (54) 54.5? | (87) 83? | | | | (67.5) 71 | (69) 77? | | | (45) 46 | (79) -90 | | | | | (64) 70.6 | (64) 67.0 | (61) 65.2 | | |
| CH ₂ =CH•CH ₂ • | 77 | 60 | 60.5 | 68.5? | | 57.5 | 54.5? | (41) 38 | | | | | (53) 50 | | (52) 58 | (45.5) 45, 48, 50 | (35) 36 | (66) 71 | (64) 64? | (83) 82 | | | (50) 54.3 | (50) 51.9 | (49) 49.9 | | |
| φ• | 104? | 94? | 94? | 101? | 110? | 88? | 83? | | (104) 103? | | | | (82) 83 | | (87) 88 | | (67) 57? | (95) 107 | (103) 94? | (119) 124? | | | | | | | |
| φ•CH ₂ • | 77 | 63 | 62 | 101? | | 59 | 54.5? | | 76.5? | | | | (58.5) 63 | (58) 63 | | (46) 50.5 | (38) 39? | (69) 73 | (63) 59 | (88) 95? | | | | | | | |
| <i>n</i> C ₄ H ₉ • | 94 | 78 | 78 | 86? | | 75 | 71? | 56.5 | 87? | | | | | | | | | | | | | | | | | | |
| (CH ₃) ₂ CH• | 89? | | | | | | | | | | | | | | | | | | | | | | | | | | |
| <i>i</i> C ₄ H ₉ • | | 74? | 73? | 81? | | 70? | 65? | | 78? | | | | | (66) 73? | (62) 75? | (55) 61? | (45) 45 | | (75) 76? | | | | (60) 69.4 | (60) 65.2 | (57) 62.2 | | |
| •Cl | | 80 | 80 | 86? | | 77 | | 58 | 88? | | | 75? | (72) 79? | (75) 85? | (60) 56.9 | | | | (90) 95? | | | (34) 37 | | | | (67.7) 73.5 | |
| •Br | | 66 | 65 | 8±4 | | | | 48 | | 50.5 | | 61? | (59) 67? | (59) 67? | | (50) 45.2 | | | (87.5) 83? | | | (27) 28 | | | | (56.5) 57 | |
| •I | | 54 | 51 | 55? | | 50 | ~46 | 36 | 57? | 39? | | ~45? | (47) 51? | (47) 51? | | | (29) 31.6 | | (71) 71? | | | | | | | (43.2) 42.4 | |
| •OH | 115~118 | 90,91 | 90,93 | 91? | | 92 | ~90 | 71 | 107? | 73 | | | 96? | (101) 102? | | | | (56) 54 | | | | | | | | (91.7) 93.6 | |
| •NH ₂ | 124~104 | 79 | 78 | | | 77 | | 64? | 94? | 59 | | 76? | (85) 89? | (95) 98? | | | | (60) 60±4 | | | | | | | | (87.7) 86.6 | |
| •CN | 121? | 110? | | 121? | | | | 92? | 124? | 95? | | | | (90) 95? | (77) 83? | (80) 71? | | | (120) 100~146 | | | | | | | | |
| •CHO | | 71~75 | 71? | 84? | | | 71? | 50? | 83? | | | | | 59? | | | | | | | | | | | | | |
| CH ₃ CO• | | 77? | 77? | | | | 77? | | | 63 | | 73? | (59) 59? | (60) 60 | (83.5) 85 | | | -90? | | | | | | | | | |
| •NO ₂ | | 57 | 52 | | | | | | | | | | | | | | | | | | | (14) 14 | | | | | |
| •NO | | | | | | | | | | | | | | | 37 | 28 | | | | | | (15) 10 | | | | | |
| •SH | | 74.2 | 73.5 | | | 72.1 | 70.6 | 54.3 | | | | 69.4 | | | | | | | | | | | | | | | |
| •SCH ₃ | >78? | 73.2 | 71.8 | | | 69.7 | 67.0 | 51.9 | | | | 65.2 | | | | | | | | | | | | | | | |
| •SC ₂ H ₅ | | 70.6 | 69.3 | | | 67.7 | 65.2 | 49.9 | | | | 62.2 | | | | | | | | | | | | | | | |

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** Szwarc, Chem. Rev., 47, 75~173, (1952).

*** Ladachi, Leigh, Szwarc, J. Proc. Royal Soc., 214, 278 (1952).

Table 2. J and e values of radicals.

| Radical | J | e | Radical | J | e | Bond energy | Radical | J | e | Bond energy | Radical | J | e | Bond energy |
|---|------|------|--|-------|-----|----------------------|---|-----|-----|--------------------|-------------------------------------|-----|-------|--|
| H• | 56 | +2.8 |  | 34(?) | 0 | $D_{R-I}=34(?)$ | BrCH ₂ • | 43 | 0 | $D_{R-H}=99$ | C ₆ H ₅ NH• | 29 | -5 | $D_{R-NH_2}\sim 48$ $D_{R^2}\sim 35$ |
| CH ₃ • | 41.5 | 0 | C ₆ H ₅ CH ₂ CH ₂ • | <32 | 0 | $D_{R-I}<47$ | Cl ₂ CH• | 27 | 0 | $D_{R-I}=42$ | (CH ₃) ₂ N• | 9 | -5(?) | $D_{R-CH_3}=50.8$ |
| C ₂ H ₅ • | 41.5 | 0 | (C ₆ H ₅) ₂ CH• | 5(?) | 0 | $D_{R-C(CH_3)_3}=28$ | Br ₂ CH• | 27 | 0 | $D_{R-I}=41$ | (CH ₃)NH• | 10 | -5(?) | $D_{R-CH_3}=52.0$ |
| nC ₃ H ₇ • | 39 | 0 | (C ₆ H ₅) ₃ C• | 19 | 0 | $D_{R-H}=75$ | I ₂ CH• | 22 | 0 | $D_{R-I}=22$ | CH ₃ O• | 40 | 0(?) | $D_{R-CH_3}=81.8$ $D_{R-COCH_3}=74.2$ |
| iC ₃ H ₇ • | 34 | 0 |  | 19 | 0 | $D_{R-H}=75$ | Cl ₃ C• | 33 | 0 | $D_{R-H}=89$ | C ₂ H ₅ O• | 27 | -5 | $D_{R^2}=30$ $D_{R-C_2H_5}=68.6$ |
| nC ₄ H ₉ • | 34 | 0 |  | | | | Br ₃ C• | 37 | 0 | $D_{R-H}=37$ | C ₃ H ₇ O• | 27 | -3(?) | $D_{R^2}=35$ |
| iC ₄ H ₉ • | 30 | -0.2 |  | 21 | 0 | $D_{R-H}=77$ | F ₃ C• | 35 | 0 | $D_{R-I}=5\sim 57$ | (CH ₃) ₃ CO• | 27 | -3(?) | $D_{R^2}=34\sim 39$ |
| CH ₂ =CH• | 50 | 0 |  | | | | ClCH ₂ CH ₂ • | 31 | 0 | $D_{R-I}=46?$ | CH ₃ S• | 30 | 0(?) | |
| CH≡C• | 63 | ? | CH ₃ -  -CH ₂ • | 20 | 0 | $D_{R-H}=76$ | ICH ₂ CH ₂ • | <32 | 0 | $D_{R-I}<47$ | C ₂ H ₅ S• | 27 | 0(?) | |
| CH ₂ =CH•CH ₂ | 20 | 0 |  | 20 | 0 | $D_{R-H}=76$ |  | 26 | 0 | $D_{R-H}=51$ | C ₆ H ₅ COO• | — | — | $D_{X_2}\sim 30$ |
| C ₆ H ₅ • | 54 | +2 | | | | | | | | | CH ₃ COO• | — | — | $D_{X_2}\sim 30$ |
| C ₆ H ₅ CH ₂ • | 23 | 0 |  | 20 | 0 | $D_{R-H}=76$ |  | 22 | 0 | $D_{R-H}=78$ | | | | |
| •CHO | 33.5 | +3.3 |  | 11 | 0 | $D_{R^2}=22$ |  | 22 | 0 | $D_{R-H}=78$ | | | | |
| CH ₃ CO• | 35 | +3.3 | | | | |  | 19 | 0 | $D_{R-H}=75$ | | | | |
| •Cl | 32 | -2 |  | 11 | 0 | $D_{R^2}=22$ |  | 20 | 0 | $D_{R-H}=76$ | | | | |
| •Br | 25 | -0.3 | | | | |  | 21 | 0 | $D_{R-H}=77$ | | | | |
| •I | 15 | +1 | CH ₂ =C-CH ₂ • | 20 | 0 | $D_{R-H}=76$ | | | | | | | | |
| •OH | 46 | -6 |  | | | | | | | | | | | |
| •NH ₂ | 44 | -5.2 | (C ₆ H ₅) ₂ C• | 5.7 | 0 | $D_{R^2}=11.4$ | | | | | | | | |
| •CN | 63 | -2.5 |  | | | | | | | | | | | |
| •NO ₂ | 12 | +1 | | | | | | | | | | | | |
| •NO | 2(?) | 0 | (C ₆ H ₅) ₂ C• | 5.7 | 0 | $D_{R^2}=11.5$ | | | | | | | | |
| •SH | 30 | 0(?) |  | | | | | | | | | | | |
| C ₆ H ₅ CO• | 30.7 | +2.5 | | | | | | | | | | | | |

Bond Energies and Reactivity of Radicals. (I)

Table 3. Average bond energy of atoms in kcal /mole

| H | C | N | O | F | Si | P | S | Cl | Ge | As | Se | Br | I | | | |
|---------------|--------------|--------------|----------------|----------------|----------------|--------------|--------------|----------------|----------------|--------------|--------------|--------------|--------------|----------|----------|----|
| 53 | 29 | 17 | 41 | 78 | 36 | 17 | 30 | 37 | 44 | 10 | 36 | 25 | 17 | <i>J</i> | | |
| +2.8 | 0 | -3.5 | -7 | -9.6 | +3.9 | +2.8 | 0 | -4 | +6 | +5 | +2 | -1.85 | 0 | <i>e</i> | <i>J</i> | |
| (98) 103.4 | (82) 87.3 | (80) 83.7 | (113) 110.2 | (158) 147.5 | (79) 75.1 | (62) 63.0 | (83) 87.5 | (102) 102.7 | (80) | (49) | (83) | (83) 87.3 | (70) 71.4 | +2.8 | 53 | H |
| | (58) 58.6 | (46) 48.6 | (70) 70.0 | (107) 107.0 | (65) 57.6 | (46) | (59) 54.5 | (66) 66.5 | (73) | (39) | (65) | (54) 54.0 | (46) 45.9 | 0 | 29 | C |
| | | (22) 20.2 | (34) — | (62) 68.8 | (66) — | (44) | (47) | (40) 38.4 | (82) | (44) | (60) | (35) | (34) | -3.5 | 17 | N |
| | | | (33) 34.9 | (52) 58.6 | (102) 89.3 | (78) | (71) | (50) 49.3 | (127) | (86) | (91) | (53) | (58) | -7 | 41 | O |
| | | | | (64) 63.5 | (148) 143.0 | (122) | (108) | (77) 86.4 | (179) | (136) | (133) | (85) | (95) | -9.6 | 78 | F |
| | | | | | (58) 42.5 | (42) | (66) 60.9 | (89) 85.8 | (57) | (27) | (64) | (68) 69.3 | (53) 51.1 | +3.9 | 36 | Si |
| | | | | | | (26) 18.9 | (47) | (65) 62.8 | (44) | (13) | (47) | (47) 49.2 | (34) 35.2 | +2.8 | 17 | P |
| | | | | | | | (60) 63.8 | (67) 66.1 | (74) | (40) | (66) | (55) 57.2 | (47) | 0 | 30 | S |
| | | | | | | | | (58) 57.5 | (105) 104.1 | (67) 60.3 | (81) 66.8 | (55) 57.2 | (54) 51.0 | -4 | 37 | Cl |
| | | | | | | | | (52) 42.5 | (24) | (58) | (80) | (63) | | +6 | 44 | Ge |
| | | | | | | | | | ×(-5) 15.1 | (36) | (44) | (27) | | +5 | 10 | sA |
| | | | | | | | | | | (68) 57.6 | (65) | (53) | | +2 | 36 | Se |
| | | | | | | | | | | | (47) 46.1 | (42) 42.9 | | -1.85 | 25 | Br |
| | | | | | | | | | | | | (34) 36.2 | | 0 | 17 | I |

Table 4. J - e and periodic table.

| | | | | | | |
|-------------------|----------------|------------|------------------|-----------------|---------------|-------------------|
| H +2.8 53 | | | | | | |
| Li +10.2 64 | Be +7 82 | B +3.4 | C 0 29 | N -3.5 17 | O -7 41 | F -9.6 78 |
| Na +11 69 | Mg +9 63 | Al +6.8 | Si +3.9 36 | P +2.8 17 | S 0 30 | Cl -4 37 |
| K +11.7 74 | Ca +10.3 | Sc +8.2 | Ti +6.2 | V | Cr | Mn |
| Cu | Zn | Ga | Ge +6 44 | As +5 10 | Se 2 36 | Br -18.5 25 |
| Rb +11.7 | Sr +10.3 | Y +8.3 | Zr +6.2 | Cb | Mo | |
| | Cd +7 25 | | Sn +5.5 | Sb +4.8 | Te +2.6 | I 0 17 |
| Cs +12.5 | Ba +11 | | | | | |
| | Hg +9 41 | | | | | |

tral base line. J and e values of atoms are shown in Table 4, Figures 1 and 2. The Figure 1 describes the contour diagram of polarity of atoms, in which the line C→S→O makes the horizontal plane with zero level and the elements in right upper corner of the diagram give the greatest negative polarity *i. e.* non-metallic group. And the elements in left under corner, which have the greatest positive polarity, are of metallic nature. In Figure 2, of the diagram of J , the elements of the first period, especially of the seventh group have similarly the high value, but the slope of J is not simple as e -slope, but it shows wave-shaped plane, in which the groups with even atomic number *i. e.* carbon and oxygen hold high position and the ones with odd atomic number *i. e.* boron, nitrogen or halogen hold low position, in other words, the latters give comparatively stable radicals. The similarity of J -diagram to the electron affinity diagram, as is shown in Figure 3, is noteworthy, which will be discussed later.

As stated above, bond energy consists of two factors, *i. e.* the covalent and the polar ones ; the former contributes in the form of sum of J values, while the latter in the form of product of e values, and this means the dual nature of atoms, unselective and selective, in condition of bonding of atoms. Two radicals with the same sign are mutually repulsive and react not easily and the positive radical reacts more easily

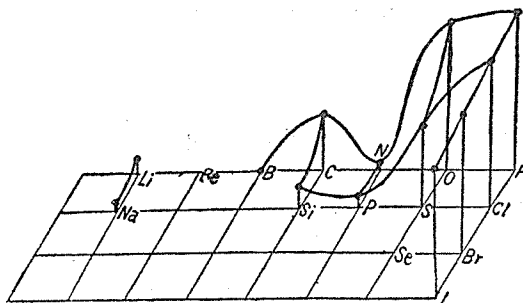


Fig. 3.

with negative one, this fact is known in inorganic compound. It is of interest that the neutral atom, for example carbon radical, has not such selective tendency and it can react not only with negative non-metallic element but also with metallic element. The importance of carbon chemistry or organic chemistry consists in the neutral nature and the high reactive nature of carbon atom. The metal alkyl as well as alkyl halide are the useful reagents in organic chemistry, which serve to make reactive carbon radical. Silicon halide or hydride, on the contrary, is not stable as alkyl halide and reactive to polar solvent, for instance to water, on account of its high positive e -value. Iodine and sulfur are also neutral atoms, but have smaller J -value than carbon; these elements act generally as the catalyst in radical reaction. Nitrogen and phosphorus, which have small J value but high negative polarity, often afford the suitable catalytic intermediate in ionic reactions, as seen in Mannich's condensation or the amine-catalysed aldol condensation. Boron or aluminium are known in their ability to make Friedel-Crafts' reagent owing to their small J -value and positive polar nature. Sodium, potassium as well as magnesium, silver or copper have the greatest positive nature and are useful in Grignard's, Wurtz's and Sandmeyer's reactions. They facilitate the formation of carbanion in polar solvent, which is considered to be generally difficult by other method.

COMPARISON OF J - e RELATION WITH PAULING'S EQUATION

Pauling's electronegativity is interpreted to be the polarization ability of atoms in the binding state *in molecules*, while the e -value in the author's equation is that *in atom* itself. These equations can be transformed to the same relation, if we put the following values into Pauling's equation,

$$\sqrt{2k} X_A = e_A, \quad \sqrt{2k} X_B = e_B$$

it follows that

$$D_{AB} = \frac{D_{AA}}{2} + \frac{D_{BB}}{2} + k(X_A - X_B)^2$$

$$= \left(\frac{D_{AA}}{2} + \frac{e_A^2}{2} \right) + \left(\frac{D_{BB}}{2} + \frac{e_B^2}{2} \right) - e_A e_B$$

Putting

$$\frac{D_{AA}}{2} + \frac{e_A^2}{2} = J_A \quad \text{and} \quad \frac{D_{BB}}{2} + \frac{e_B^2}{2} = J_B ,$$

the author's equation can be derived. It is worth considering that J -values are affected by the way of determination of e -values. It is in Pauling's equation unnecessary. The Tables 2 and 3 are made by taking the e -value of carbon as zero.

In Pauling's relation, it is easily understood, that the polarization in bond A-B is proportional to $(X_A - X_B)$ and the electro-static potential energy between the charges of $+(X_A - X_B)$ and $-(X_A - X_B)$ is equal to $(X_A - X_B)^2/r$, where r is the distance between both the atoms. It is supported by the proportionality of dipole moment with the difference between electronegativities of atoms. The meaning of author's relation is not yet elucidated, but the following interpretation is probably valuable. In an atom with negative e -value, the polarization is also occurred as seen in molecules. Figure 4 describes such polarization, in which $-q_A$ is the negative charge in nucleus and $+q_A$

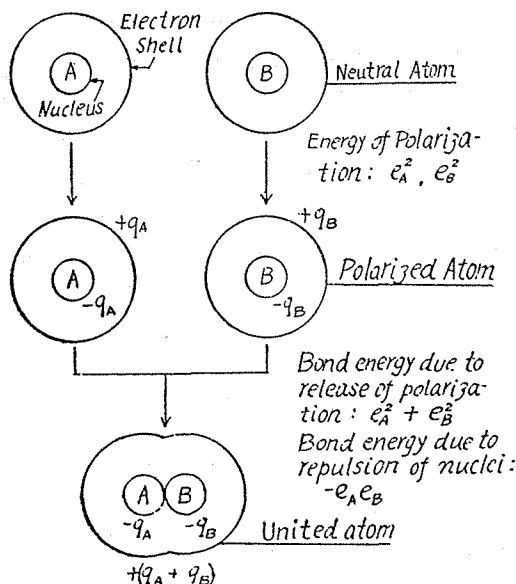


Fig. 4.

in electron shell. Such polarization affects the bond energy in two different ways. One is the contribution to the coulombic energy between two atoms, which corresponds to $q_A^2/2r_1$, where r_1 is the radius of the atom. And the other is the moderation of the polarization in atom caused by mixing of the electron cloud of both atoms or overlapping of both the electron shell. Such effect is similar to the entropy increase

caused by mixing of gas in two boxes. The polarization energy of atom can be calculated supposing the structure similar to the double sphered electric condenser; the inner sphere corresponds to nucleus and the outer the electron shell. The polarization energy E of such condenser is given as follows:

$$E = \frac{1}{2} q_A^2 / C$$

where C is the capacity of the condenser and is equal to

$$C = 1 / (1/r_1 - 1/r_2),$$

and r_1 and r_2 are the radii of the inner and the outer spheres respectively. If $r_1 \ll r_2$, it follows that

$$C \cong r_1$$

and
$$E = \frac{1}{2} q_A^2 / r_1$$

Such polarization *i. e.* the electric strain may be moderated when the outer shells of the both atoms are mutually shared, as seen in Figure 4 and the electric strain decreases to the half. Consequently the contribution of polarization to bond energy is regarded to be a half of the polarization energy of atom, *i. e.* $q_A^2/4r_1$. If $q_A/\sqrt{2}r_1$ is equal to e_A , and $q_B/\sqrt{2}r_1$ to e_B , it follows that

$$\begin{aligned} D_{AB} &= \left(\frac{D_{AA}}{2} + \frac{q_A^2}{4r_1} \right) + \left(\frac{D_{BB}}{2} + \frac{q_B^2}{4r_1} \right) - \frac{q_A q_B}{2r_1} \\ &= \left(\frac{D_{AA}}{2} + \frac{e_A^2}{2} \right) + \left(\frac{D_{BB}}{2} + \frac{e_B^2}{2} \right) - e_A e_B \end{aligned}$$

The terms $D_{AA}/2$ and $D_{BB}/2$ are regarded as the bonding ability due to the valency electron of atoms A and B respectively. The detailed discussion will be presented in subsequent paper.

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